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Application to long term disposal of nuclear wastes

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Abstract

In pressurised water reactors the cladding tubes in zircaloy-4 are oxidised up to several micrometers on the internal face by direct contact with the UO_2 pellets. At the same time, fission products such as ^{129}I are implanted by recoil. Until 1995, the cladding tube pieces called hulls were embedded in concrete. The concrete medium being very basic, this study simulates the corrosion of hulls in the perspective of a long term disposal in these severe pH conditions. This paper is dedicated to the study of the partial dissolution of the oxide layer, which is the responsible mechanism for the activity release. In order to follow the solid-liquid interface, europium was implanted into the material surface as a marker. Next, the corrosion induced in autoclave at 300°C, 140 bars and in alkaline water was studied. The determination of europium profiles using Rutherford Backscattering Spectrometry analysis (RBS) allows to deduce the fraction of dissolved ZrO_2. It was shown that this dissolution is not homogeneous in porous zirconia and gives rise to the formation of crevices. Using the

nuclear microprobe of Pierre Süe laboratory, a more precise study of the specimen surface was performed.

1. Introduction

During Pressurised Water Reactor operation, the cladding tubes get oxidised on both the inner side and the external side. The external oxidation of about 100 µm thickness is due to the contact with the cooling water and has been largely studied [1,2]. The internal oxidation due to the contact with the UO_2 fuel is much thinner (about 10 µm) and has been rarely taken into account [3, 4]. During reprocessing the cladding tubes are cut up and washed with nitric acid to dissolve the spent fuel. Considering that fission products are implanted by recoil in this oxide layer and remain implanted in the hulls (cladding tube pieces) even after reprocessing, it is important to study the dissolution of this zirconia layer in the hypothesis of a geological disposal. Until 1995, the hulls were embedded in concrete. The concrete medium being very basic, this study simulates the corrosion of hulls in these severe pH conditions. This paper is thus related to the long term behaviour of hulls subject to a corrosive environment and to the release of a specific fission product which is iodine. It will present dissolution experiments on zirconia, performed in autoclave during various times and analysed using both a standard RBS set up and a microprobe facility.

2. Experimental procedure

2.1 Samples

Zircaloy-4 pellets (1.7 wt% Sn, 0.24 wt% Fe, 0.13 wt% Cr) were used. It is well known that the oxidation kinetics of zirconium presents two parts: the first one is parabolic or cubic whereas the second one is linear. They respectively correspond to the formation of compact or porous zirconia [5]. These two types of zirconia were prepared from our samples.

They are either a thin compact zirconia layer of 1 µm thick prepared by annealing in air for 3 hours at 500°C or a thicker porous one (18 µm thick) obtained by annealing 40 hours in air at 600°C. In order to determine the dissolution kinetics of zirconia, an europium implantation was performed on

each sample as a surface marker. A previous study [6] has shown that the diffusion coefficient of this species is negligible in zirconia at 300°C and that consequently any Eu release will be significant for a zirconia dissolution. The samples were implanted with 200 keV ^{153}Eu ions, at a fluence of 10^{16} ions cm^{-2}, on the isotope separator of the 'Institut de Physique Nucléaire' of Lyon (IPNL). According to the SRIM code [7], the mean range is 42 nm and the straggling is 16 nm. Iodine was chosen as a representative volatile fission product and well known for its very long half life (T = 1.6x10^7 years). ^{127}I was implanted at 180 keV and at a fluence of 10^{16} ions cm^{-2} in order to superimpose the iodine and europium profiles.

2.2 Corrosion tests

Corrosion tests were performed in autoclave. The specimens were exposed to a 300°C basic solution under a 140 bars pressure. The basic solution was representative of infiltrated water though a concrete media. This solution was prepared with sodium hydroxide (2.867 g/l) and potassium hydroxide (16.830 g/l). The resulting pH of this solution at 25°C was 13.5. The corrosion tests were conducted during 12 weeks with regular samplings every two weeks.

2.3 Surface Analysis

At each step of the corrosion tests, the europium and iodine profiles were measured by classical RBS using 3.06 MeV alpha backscattering on the 4 MV Van de Graaff accelerator of the IPNL. Some samples were also analysed on the nuclear microprobe facility of the Pierre Süe Laboratory in Saclay, previously described by Revel and Duraud [8]. The ^{4}He$^+$ beam was

focused down to 9 μm^2 and the spot intensity was limited to 250 pA. Scattered ions were detected with an annular surface barrier detector. The sensitivity is much less with the microbeam due in particular to the low integrated charge. It is however compensated by the very good lateral resolution.

3. Results

3.1 Dissolution kinetics of zirconia

This dissolution has been studied thanks to the europium marker. As previously mentioned, Eu does not diffuse in zirconia at 300°C. We found [6] that the activation energy of Eu in zirconia was 2.5 eV at^{-1} and that the Eu diffusion coefficient at this temperature was $2x10^{-27} cm^2\ s^{-1}$. Such a value means that, within 70 days, Eu would migrate of $2x10^{-3}$ nm.. Consequently any Eu release observed in the present experiments can only be due to a zirconia dissolution and not to a diffusion mechanism. After various stays in autoclave, the europium implanted pellets (compact and porous zirconia) were analysed by classical RBS. The europium concentration profiles deduced from these spectra are given in figure 1. From this figure, three main observations can be made as the corrosion time is increasing: i) the decrease of the maximum of the Eu distributions, ii) a smooth translation of the europium distributions towards the surface, iii) a decrease of the Eu global concentrations. From these data, we deduce that a non homogeneous dissolution of the zirconia layer occurs in this alkaline medium. The RBS analysed area is roughly 1 mm^2 which allows to deduce a mean value of the dissolution kinetics illustrated in figure 2. This evolution is linear and the slope gives a dissolution rate of 1 nm per day. This behaviour is found to be the same in compact and porous zirconia.

3.2 Iodine behaviour in basic solution

The iodine implanted samples were submitted to the same autoclave treatment as the europium ones. They were also analysed by classical RBS. The iodine profile evolution is given in figure 3 for the 14 and 28 days of corrosion time in comparison with the as-implanted sample (compact zirconia). In the first 14 days the iodine release reaches 80% and then remains stable. This loss is thus much more important compared to the europium one (14%) in the same conditions and consequently is much more rapid than the zirconia dissolution. Hence, this iodine release is not due to this zirconia dissolution but to another mechanism. Similar experiments performed in porous zirconia show the same results.

3.3 Homogeneity of the zirconia dissolution

In order to study the dissolution mechanisms, the europium implanted samples were analysed with a microprobe facility. Results presented here concern the samples treated 14 days in autoclave. Above these duration, the europium concentrations became too low to be detected. It is to be noted that the iodine concentrations being even weaker, it was not possible to determine their evolution with the microbeam. Using an optical microscope coupled to the microprobe, different zones were observed on the porous zirconia surface showing that this surface is not homogeneous. Holes and flat areas are observed and were selectively analysed by the microbeam. Figure 4 compares the europium concentration profiles in a hole and in flat zone. A difference of 19 % in europium concentration is observed between these two spots. The analysis of the compact structure reveals a more homogeneous surface state. Using the microbeam, no variation of europium concentration has been put in evidence.

4. Discussion

The results obtained using classical RBS have allowed to determine a dissolution rate of 1 nm per day both in compact and porous zirconia. The lateral resolution of the technique

being 1 mm^2, no difference in the dissolution rate is observed to such a scale. However, the surface topography is found to be significantly different in these two structures, the porous zirconia presenting kinds of holes. By measuring a preferential loss of europium at the surface of porous zirconia, the use of a microbeam put in evidence a non homogeneous dissolution of this structure. In addition, during the first 14 days in autoclave, it was shown in millibeam experiments, that almost all the iodine is removed from the sample surface. Since the iodine loss is not related to the zirconia dissolution, its origin can correspond i) to an enhanced diffusion or ii) to the formation of a volatile compound, containing potassium or sodium for example, which would dissolve in the solution or iii) to an ion exchange process I^-/OH^-. We have first compared our results with a recent study [9] of iodine diffusion in Zr by air annealing between 700 and 900°C. In that work, apparent diffusion coefficients were deduced from RBS measurements. Making a linear extrapolation of these data, a coefficient of $2x10^{-29}$ cm^2 s^{-1} is found at 300°C. Considering this value, the diffusion phenomenon cannot explain the observed rapid iodine release. Since PIXE experiments using the microbeam did not allow to detect the presence of K or Na species on the sample surface, the formation of soluble KI or NaI compounds is unlikely. The last hypothesis of ion exchange in the basic medium very rich in OH^- species seems to be the most probable explanation. Similar experiments are now being performed with pure water in order to help the interpretation of the present results.

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References

[1] C. Lemaignan and A.T. Motta, Materials and technology edited by R.W. Cahn, P. Haasen and E.J. Kramer, 10B, 1994.

[2] IAEA, Waterside corrosion of zirconium alloys in nuclear power plants, austria, 1998.

[3] R. Restani, E.T. Aerne, G. Bart, H.P. Linder, A. Müller, F. Petrik, Technical Report 92-13, Nagra, Wettingen, Switzeland, 1992.

[4] Hj. Kleykamp, J. Nucl. Mater. 171 (1990)181.

[5] P. Barberis, J. Nucl. Mater., 226 (1995) 34.

[6] K. Poulard, A. Chevarier, J.C. Duclot, N. Moncoffre, D. Crusset, Nucl. Instr. And Meth. in Phys. Res. B 161-163 (2000) 668.

[7] J.F. Ziegler, J.P. Biersack, U. Littmark, The stopping and Range of Ions in Solids, Pergamon Press, New York,1985.

[8] G. Revel and J.P. Duraud, Les Techniques de l'Ingénieur, P2563 (1995) 1.

[9] F. Brossard, N. Chevarier, N. Moncoffre, Ph. Sainsot, D. Crusset, H. Jaffrezic, J. Nucl. Mat, 279 (2000) 153.

Figure captions

Figure 1 : Evolution of the 200 keV europium concentration profiles at 300°C as function of the annealing time in autoclave.

Figure 2 : Dissolution kinetics of zirconia in a basic solution, in autoclave at 300°C.

Figure 3 : Evolution of the 180 keV iodine concentration profiles at 300°C as function of the annealing time in autoclave.

Figure 4 : Eu concentration profiles in porous zirconia after 14 days in autoclave, as function of the analysed spot.

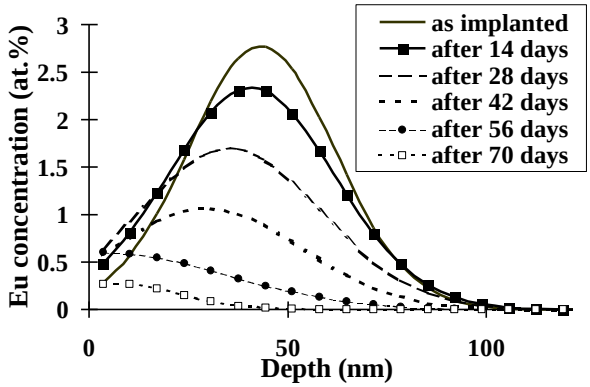

Figure1

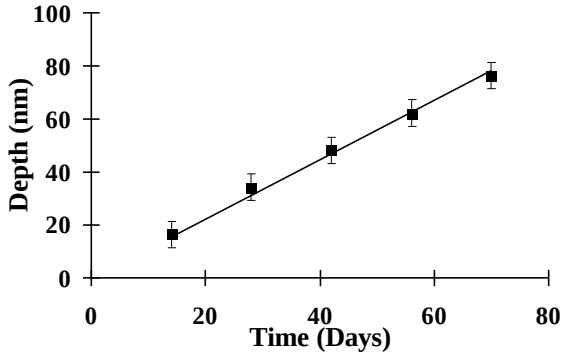

Figure 2

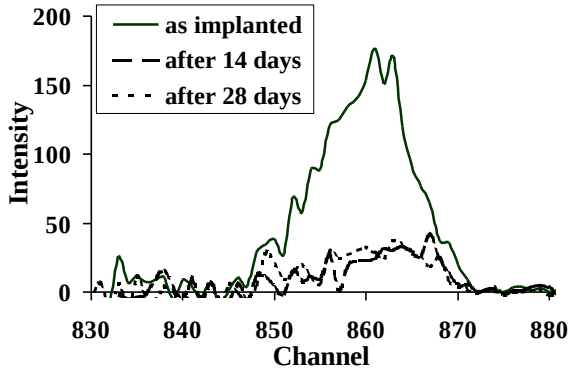

Figure 3

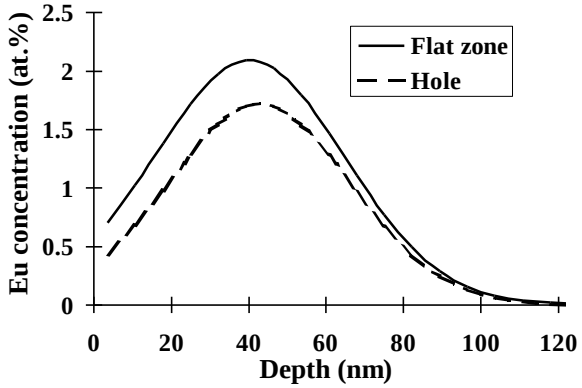

Figure 4